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(21) International Application Number: PCT/GB93/02464 (22) International Filing Date: 30 November 1993 (30.11.93) (30) Priority Data: 9225540.5 7 December 1992 (07.12.92) GB (71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chemical House, Millbank, London SW1P 3JF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): MITCHELL, Christopher, John [GB/GB]; 39 Marina Village, Runcorn, Cheshire WA7 3BH (GB). WINTERTON, Neil [GB/GB]; Copper Pine, Carmel Hill, Pantasaph, Holywell, Clwyd CH8 8NZ (GB). (74) Agents: THOMAS, Ieuan et al.; ICI Group Patents Services Dept., P.O. Box 6, Shire Park, Welwyn Garden City, Hertfordshire AL7 1HD (GB).		(81) Designated States: AU, BR, CA, FI, JP, KR, NO, NZ, PL, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CLEANING COMPOSITIONS (57) Abstract An article may be cleaned by (i) contacting it with a substantially non-aqueous cleaning composition which comprises a dipolar aprotic or protic organic compound, an aliphatic compound and a surfactant and which is preferably in the form of a non-aqueous microemulsion and (ii) removing residual substantially non-aqueous cleaning composition from the article by contacting it with an aqueous rinsing medium.		

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CLEANING COMPOSITIONS

The present invention relates to cleaning compositions, particularly cleaning compositions in which contaminated articles such as, for example, metals, glass, electronic components and printed circuit boards, are contacted with a cleaning composition and the residual cleaning composition is removed from the articles by rinsing in water.

Solvent cleaning applications wherein contaminated articles are immersed in or washed with halogenated hydrocarbon solvents and/or the vapours thereof are well known and are in common use.

It is now widely recognised that certain chlorine-containing compounds, particularly chlorofluorocarbons, may be damaging the ozone layer surrounding the earth and it has been agreed that the manufacture and use thereof should be severely restricted and eventually curtailed.

Non-halogenated solvents, eg terpenes, have been proposed as substitutes for halogenated hydrocarbon solvents in US 4,640,719. However, terpenes are often completely insoluble in water and cannot be directly flushed away thereby and it has been further proposed therein to incorporate one or more emulsifying surfactants with water to facilitate removal of the terpene from the article. Recently, mixtures of hydrocarbons and dibasic esters, often in the presence of a so-called compatibilising component, and mixtures of aliphatic hydrocarbons and certain polar organic compounds have been proposed as cleaning solvents for certain applications in EP 0,412,475 and WO 91/06690 respectively. The aforementioned mixtures tend to suffer from certain disadvantages, e.g. one or more components thereof cannot be recycled, is toxic or is flammable.

Multi-component mixtures including terpenes, N-methylpyrrolidinone (CAS 872-50-4; hereinafter referred to for convenience as "NMP") and various additives have

been proposed as cleaning compositions for certain applications in Research Disclosure, January 1988, 44, No 28555, EP 0,354,027 and US 4,983,224; and cleaning compositions comprising NMP, a water-miscible
5 alkanolamine and a hydrocarbon have been proposed in US 4,276,186.

Certain aqueous microemulsions for use in cleaning systems have been disclosed in WO 92/03528, WO 90/02665, US 5,230,821, US 5,171,475, US 5,112,516, US 5,213,624
10 and US 5,158,710.

WO 93/13246 discloses mixtures of a C_8-C_{15} hydrocarbon and a C_5-C_{15} aliphatic alcohol for use as cleaning solvents. WO 93/03102 discloses the cleaning of the surfaces of solid articles by wiping with a rag
15 containing a mixture of propylene glycol methyl ether acetate and at least one of propylene glycol methyl ether, methyl isoamyl ketone, isoparaffin and n-butyl acetate.

US 4,867,800 and US 4,983,224 discloses certain cleaning compositions derived from terpene hydrocarbons.
20 US 5,011,620 discloses certain cleaning compositions derived from dibasic esters.

We have now invented a non-halogenated solvent suitable for cleaning applications which is ozone benign, non-corrosive, non-combustible and has low toxicity.
25

By "non-combustible" we mean that the solvent has a flash point above about 60°C measured by the Tag Closed Cup method.

According to the first aspect of the present invention there is provided a substantially non-aqueous cleaning composition which comprises a dipolar aprotic or
30 protic organic compound, an aliphatic compound and a surfactant.

According to a preferred aspect of the present invention the non-aqueous cleaning composition is in the form of a non-aqueous microemulsion.
35

By "non-aqueous microemulsion" we mean a combination of a first organic liquid and a second organic liquid substantially immiscible therewith which are mixed in the presence of a surfactant such that an optically clear, optically isotropic liquid is formed. Typically, such microemulsions have low viscosity and small domain size and are thermodynamically stable.

Non-aqueous microemulsions wherein the first organic liquid is formamide have been studied (Lattes et al, Colloids Surf, 1989, 35, 221-35; Friberg et al, Langmuir, 1988, 4, 796-801; Das et al, J Phys. Chem. 1987, 9, 2 938-2946; Warnheim et al, J. Coll. Int. Sci., 1989, 131, 402-8), particularly as a medium for organic synthesis (Rico et al, J Amer. Chem. Soc., 1989, III, 7266-7; Rico et al, J Chem. Soc. Chem. Comm., 1987, 1205-6) and non-aqueous microemulsions wherein the first organic liquid is glycerol have been reported (Friberg et al, Surf. Sci. Ser. 24 (Microemulsion Systems); Fletcher et al, J. Chem. Soc. Faraday Trans., I, 1984, 80, 3307-14; Martino et al, J. Phys. Chem. 1990, 94, 1627-1631).

As examples of dipolar aprotic or protic solvents of which the cleaning composition according to the present invention may be comprised may be mentioned inter alia glycols, eg ethylene glycol; amides, eg dimethyl formamide; sulphoxides, eg dimethyl sulphoxide; or preferably an N-alkyl pyrrolidinone, more preferably NMP.

The aliphatic compound of which the cleaning composition according to the present invention may be comprised has a flash point of more than 60°C and boils in the range 150-300°C, preferably in the range 180-275°C.

The aliphatic compound is preferably an alkane, more preferably a C₁₀₋₁₃ alkane or a mixture thereof and particularly more preferably dodecane. We do not exclude the possibility that the aliphatic compound may contain one or more rings, eg it may a "naphthene" derivative,

i.e. "naphthenic"; however, this is not preferred.

We do not exclude the possibility that the aliphatic compound may bear one or more substituents which do not unduly inhibit the solvent power of the aliphatic compound or unduly increase its miscibility/compatibility with the dipolar aprotic or protic organic compound, eg NMP, or its stability to the operational conditions in which the cleaning composition may be used.

We do not exclude the possibility that the cleaning composition of the present invention may contain a small amount, up to about 5% w/w say, of an aromatic compound, although this is not preferred.

The surfactant in the non-aqueous cleaning composition according to the present invention is preferably a non-ionic surfactant, although we do not exclude the possibility that an ionic surfactant, e.g. a cationic or an anionic surfactant, may be used.

As examples of suitable non-ionic surfactants may be mentioned inter alia surfactants derived by the alkoxylation, eg ethoxylation, of a hydroxy-containing compound, eg a phenol, sugar, or preferably an alcohol. It is often preferred that the non-ionic surfactant is an ethoxylated long-chain alcohol.

By "long-chain alcohol" we mean an alcohol having between 7 and 20 carbon atoms, preferably between 9 and 15 carbon atoms. Conveniently a mixture of C_9 and C_{11} alcohols is used. The long-chain is preferably linear although we do not exclude the possibility that it may be branched, e.g. a 2-methyl isomer.

Where the surfactant is derived from an ethoxylated long-chain alcohol the ratio of the number of ethoxy groups to the length of the alcohol chain in the surfactant will be chosen in the light of inter alia the dipolar aprotic or protic organic compound and the aliphatic hydrocarbon present in the cleaning composition. The skilled man, by simple experiment, will

be able to determine a suitable ratio of the number of ethoxy groups to the length of the alcohol chain in the surfactant.

The concentration or ratio of dipolar aprotic or protic organic compound, aliphatic compound and surfactant in the non-aqueous cleaning composition according to the preferred aspect of the present invention may vary within wide limits but the mixture should contain sufficient surfactant to render the cleaning composition clear to the naked eye.

Where the dipolar aprotic or protic organic compound is NMP the concentration of the non-ionic surfactant is typically between 5 and 50 w/w%, preferably between 10 and 25 w/w%; the concentration of NMP is between 2 and 30 w/w%, preferably between 5 and 20 w/w%; and the concentration of the aliphatic compound is between 50 and 95 w/w%, preferably between 60 and 80 w/w%, wherein the sum of %w/w's of the aforementioned components is 100%.

According to a preferred embodiment of the present invention the concentration of the non-ionic surfactant is about 18% w/w, the concentration of the dipolar aprotic or protic organic compound is about 12% w/w and the concentration of the aliphatic compound is about 70% w/w, particularly where the non-ionic surfactant is Synperonic (RTM) 91/2.5, the dipolar aprotic or protic organic compound is NMP and the aliphatic compound is dodecane.

According to a further preferred aspect of the present invention there is provided a non-aqueous cleaning composition in the form of a micremulsion comprising a surfactant, an aliphatic compound and a dipolar aprotic or protic organic compound in the proportions falling within the cross-hatched area shown in the diagram of Figure 1.

According to a yet further preferred aspect of the present invention there is provided a non-aqueous

cleaning composition in the form of a microemulsion comprising a surfactant, an aliphatic compound and a dipolar aprotic or protic organic compound in the proportions falling within the shaded area shown in the diagram of Figure 2.

We do not exclude the possibility that in addition to the dipolar aprotic or protic organic compound, the aliphatic compound and the non-ionic surfactant the cleaning composition may contain additives, for example a stabiliser, or a corrosion inhibitor.

The cleaning composition may be used in cold cleaning applications but will typically be employed at an elevated temperature up to its flash point. Cleaning is conveniently carried out at about 20-55°C.

According to a further aspect of the present invention there is provided a process for the cleaning of an article which process comprises the step of contacting the article with the cleaning composition according to the first aspect of the present invention, for a suitable period of time, removing the article from contact with the cleaning composition and rinsing the article with an aqueous medium to remove residual cleaning composition therefrom.

The method of contacting the article with the cleaning composition in the process according to the further aspect of the present invention is not critical. For example, the article, or an appropriate portion thereof, may be contacted with the liquid cleaning composition, typically by immersion in a bath thereof. However, we do not exclude the possibility that the article may be subjected to a spray of the cleaning composition or the cleaning composition may flow over the stationary article. In a further embodiment the article is subjected to ultrasonic radiation or mechanical agitation, e.g. stirring or vibration, during the contacting step.

The article is removed from contact with the cleaning composition, eg by removing the article from a bath of the liquid cleaning composition, and residual cleaning composition thereon is removed by rinsing with an aqueous rinsing medium. Typically, the aqueous rinsing medium is water. Rinsing is conveniently carried out at 20-55°C, e.g. ambient temperature.

The cleaning composition is preferably recovered from the liquid mixture produced in the rinsing step and recycled.

The article cleaned in the process of the present invention is typically an electronic component. For example, flux residues may be removed from a printed circuit board after soldering.

The present invention is further illustrated by reference to the accompanying drawings which show, by way of example only, certain compositions useful in the present invention.

In the drawings:

Figure 1 is a phase diagram for systems containing dodecane, Synperonic (RTM) 91/25 and NMP;

Figure 2 is a part of the phase diagram shown in Fig 1 to a bigger scale; and

Figure 3 is a phase diagram for systems containing dodecane, a propoxylated surfactant and NMP.

In Figures 1, 2 and 3, the optically clear compositions are indicated by the hatched portions 1; portions 2 indicate two-phase compositions.

In Figures 1 and 2, the cross-hatched portion 3 indicates preferred compositions; and in Figure 2, the shaded portion 4 indicates more preferred compositions.

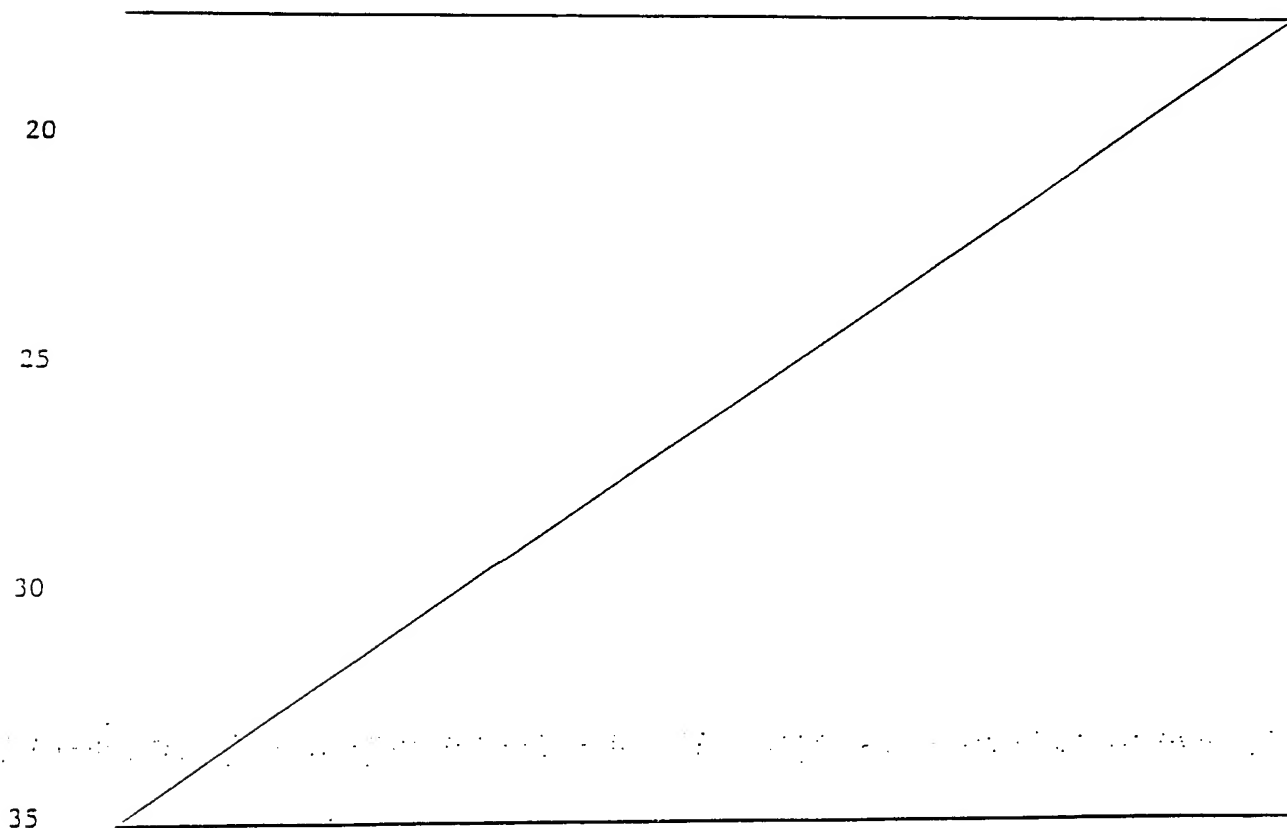
Examples 1-6

Examples 1-2 illustrate cleaning compositions according to the present invention; Examples 3-6 are Comparative Tests.

In Examples 1 and 2, NMP was added to a 20% w/w Synperonic 91/2.5 (ex ICI; Synperonic is an RTM)/dodecane mixture to give the cleaning compositions shown in the Table.

5 Test boards to which approximately 0.6g of Multicore PRAB 3 Solder Cream had been applied and then reflowed in a Micro Vapour Phase Soldering Unit were individually immersed and gently agitated in the solvent shown in the Table at 35°C for 3 minutes. The test boards were then rinsed in deionised water for 1 minute at room
10 temperature and dried using compressed air. Residual ionic contamination was measured using a Protonique Contaminometer.

The results are shown in the Table from which it can be seen that higher flux removal and boards of better
15 appearance were obtained in Examples 1 and 2 than in the Comparative Tests.



TABLE

Example No	Cleaning Composition % w/w			Flux Residues Removed %	Appearance of Test-Board after Cleaning
	Dd	Syn	NMP		
1	74	18.5	7.5	96	No rosin on test-board
2	68	17	15	96	"
CT3	100	0	0	48	Traces of rosin on test-board
CT4	90	10	0	85	"
CT5	80	20	0	88	"
CT6	70	30	0	89	"
Dd: Dodecane Syn: Synperonic (RTM) 91/2.5					

CLAIMS

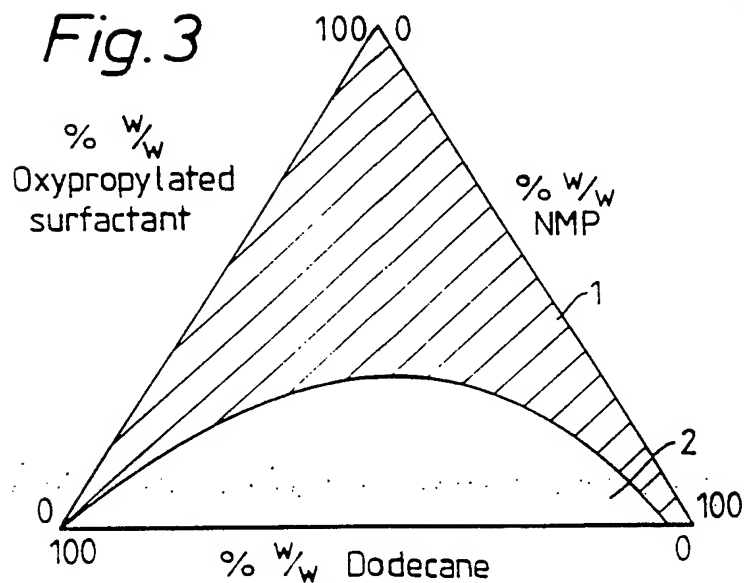
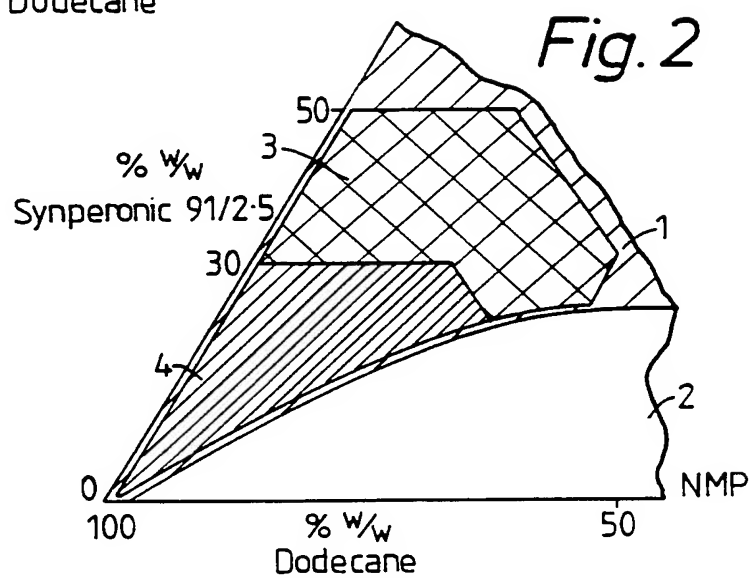
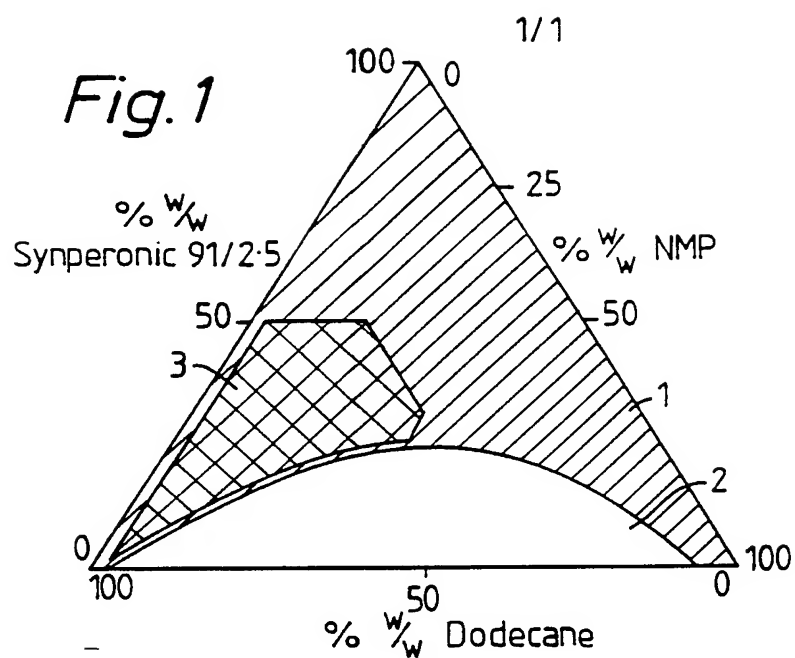
1. A substantially non-aqueous cleaning composition which comprises a dipolar aprotic or protic organic solvent, an aliphatic compound and a surfactant.
2. A substantially non-aqueous cleaning composition as claimed in Claim 1 in the form of a microemulsion.
3. A substantially non-aqueous cleaning composition as claimed in Claim 1 or 2 wherein the dipolar aprotic or protic organic solvent is an N-alkyl pyrrolidinone.
4. A substantially non-aqueous cleaning composition as claimed in Claim 3 wherein the N-alkyl pyrrolidinone is N-methyl pyrrolidinone.
5. A substantially non-aqueous cleaning composition as claimed in Claim 1 wherein the aliphatic compound is a C₁₀-C₁₃ alkane.
6. A substantially non-aqueous cleaning composition as claimed in Claim 5 wherein the C₁₀-C₁₃ alkane is dodecane.
7. A substantially non-aqueous cleaning composition as claimed in Claim 1 wherein the surfactant is a non-ionic surfactant.
8. A substantially non-aqueous cleaning composition as claimed in Claim 7 wherein the non-ionic surfactant is an ethoxylated long-chain alcohol.
9. A substantially non-aqueous cleaning composition as claimed in Claim 8 wherein the ethoxylated long-chain alcohol is a Synperonic (RTM).

10. A substantially non-aqueous cleaning composition as claimed in Claim 4, wherein the concentration of the NMP is between 5%w/w and 20%w/w, the concentration of the aliphatic compound is between 60%w/w and 80%w/w and the concentration of the non-ionic surfactant is between 10%w/w and 25%w/w.

11. A substantially non-aqueous cleaning composition as claimed in Claim 4, 6 or 9 wherein the concentration of the NMP is about 12%w/w, the concentration of the dodecane is about 70%w/w and the concentration of Synperonic (RTM) 91/2.5 is about 18%w/w.

12. A process for cleaning an article, or a portion thereof, comprising the step of contacting it with the substantially non-aqueous cleaning composition claimed in any one of Claims 1-11 at about 20-55°C.

13. A process as claimed in Claim 12 comprising the further step of removing residual substantially non-aqueous cleaning composition from the article by rinsing it with an aqueous rinsing medium.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/02464

A. CLASSIFICATION OF SUBJECT MATTER

C 11 D 3/44, C 11 D 3/28, C 11 D 3/18, C 11 D 1/72,
C 11 D 17/00, C 23 G 5/06, C 23 G 5/024, C 23 G 5/036

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 11 D, C 23 G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A1, 91/06 690 (HENKEL) 16 Mai 1991 (16.05.91), page 3, lines 16-30; page 5, lines 5-15; claims 1-5, 8, 10 (cited in the application). --	1, 3-6, 10
Y	DE, A1, 3 728 547 (COLGATE-PALMOLIVE) 03 March 1988 (03.03.88), abstract; example 1(1, 9, 11, 14, 15, 22). --	1, 2, 5- 9
Y	US, A, 4 764 222 (COLEGROVE) 16 August 1988 (16.08.88), the whole document. --	1, 3, 4
A	US, A, 4 428 871 --	1, 3, 4



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	(WARD et al.) 31 January 1984 (31.01.84), table 1. -----	

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
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international n°

PCT/GB 93/02464 SAE 82373

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